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SOLDER ALLOY, USE OF THE SOLDER ALLOY AND METHOD FOR PROCESSING, PARTICULARLY REPAIRING, WORKPIECES, PARTICULARLY GAS TURBINE COMPONENTS

FIELD OF THE INVENTION

The present invention relates to a solder alloy as well as a multi-component soldering system. Furthermore, the present invention relates to the use of a solder alloy and of a multi-component soldering system as well as to a method for processing, e.g., repairing, workpieces, e.g., of gas turbine components.

BACKGROUND INFORMATION

Gas turbines, as for example aircraft engines or stationary gas turbines, in operation are subject to high mechanical and thermal stress. Thus, during the operation of an aircraft engine, blades, e.g., turbine blades, may be damaged by alternating thermal stress and material removal. This results in thermal fatigue cracks and eroded surfaces, which must be completely and reliable repaired when servicing or repairing the aircraft engine. For this purpose, conventionally, soldering methods are used in addition to welding methods.

In this connection, conventionally, soldering methods and solder materials are uses as described in U.S. Patent No. 4,830,934 and U.S. Patent No. 5,240,491, for example. These conventional soldering methods are used for repairing the above damage symptoms and as joining processes in the manufacture of an aircraft engine. Since following the repair, the subassemblies of an aircraft engine are again exposed to high mechanical and thermal stress, it is necessary to provide novel solder alloys and soldering methods.

SUMMARY

Example embodiments of the present invention may provide a solder alloy as well as a multi-component soldering system. Example embodiments of the present invention may further provide a use for such a solder alloy and such a multi-component soldering system and a method for processing, e.g., repairing, workpieces, e.g., gas turbine components.

According to an example embodiment of the present invention, the solder alloy is a nickel-based alloy and includes at least the following elements: chromium (Cr), cobalt (Co), molybdenum (Mo) and nickel (Ni). The molybdenum (Mo) replaces the tungsten (W) using in conventional solder alloy. By mixed crystal hardening, molybdenum (Mo) increases the strength of the γ-nickel matrix, without, however, disadvantageously increasing the melting point of the solder alloy to the same extent as tungsten (W).

The solder alloy may additionally include tantalum (Ta), niobium (Nb) and aluminum (Al). This may achieve an additional strength by particle hardening effects. Tantalum (Ta), niobium (Nb) and aluminum (Al) are γ′-forming elements.

In this connection, the following composition of the solder alloy may be provided:

- chromium (Cr) in a proportion of 5 – 17 wt.%,
- cobalt (Co) in a proportion of 8 – 15 wt.%,
- molybdenum (Mo) in a proportion of 1 – 5 wt.%,
- aluminum (Al) in a proportion of 2 – 8 wt.%,
- tantalum (Ta) in a proportion of 1 – 8 wt.%,
- niobium (Nb) in a proportion of 0.1 – 2 wt.%,
- nickel (Ni) in a residual proportion such that the sum of all portions yields 100 wt.%.

The solder alloy may additionally include palladium (Pd) in a proportion of 0.5 to 5 wt.% and boron (B) in a proportion of 0.5 to 2.5 wt.%.

Palladium (Pd) lowers the melting point of the solder alloy and increases the strength of the γ-nickel matrix by mixed crystal hardening. Furthermore, it may be provided that palladium (Pd) improves the wetting behavior and the fluidity of the molten solder alloy or of the molten multi-component soldering system.

In this connection, the following composition of the solder alloy may be provided:

- chromium (Cr) in a proportion of 5 - 17 wt.%,
- cobalt (Co) in a proportion of 8 - 15 wt.%,
- molybdenum (Mo) in a proportion of 1 - 5 wt.%,
- aluminum (Al) in a proportion of 2 - 8 wt.%,
- tantalum (Ta) in a proportion of 1 - 8 wt.%,
- niobium (Nb) in a proportion of 0.1 - 2 wt.%,
- palladium (Pd) in a proportion of 0.5 - 5 wt.%,
- boron (B) in a proportion of 0.5 - 2.5 wt.%,
- nickel (Ni) in a residual proportion such that the sum of the portions yields 100 wt.%.

The solder alloy may additionally include yttrium (Y) in a proportion of 0.1 to 1 wt.% and hafnium (Hf) in a proportion of 1 to 5 wt.%. Like Palladium (Pd), hafnium (Hf) may improve the wetting behavior and the fluidity of the molten solder alloy or of the molten multi-component soldering system and increases at the same time the oxidation-resistance of the soldered regions. In order to keep the portion of hafnium-containing hard phases low, which may embrittle the solder structure, the hafnium portion is limited to 5 wt.%.

Like palladium (Pd) and boron (B), yttrium (Y) may lower the melting point or the melting range of the solder alloy such that soldering temperatures may be set specifically in the range of 1200 °C to 1260 °C by the combination of elements Pd-B-Y.

The melting range is defined as the temperature interval between the melting of the first alloy components (solidus point) and the completely liquid state (liquidus point) of the particular alloy.

In this connection, the following composition of the solder alloy may be provided:

- chromium (Cr) in a proportion of 5 - 17 wt.%,
- cobalt (Co) in a proportion of 8 - 15 wt.%,
- molybdenum (Mo) in a proportion of 1 - 5 wt.%,
- aluminum (Al) in a proportion of 2 - 8 wt.%,
- tantalum (Ta) in a proportion of 1 - 8 wt.%,
- niobium (Nb) in a proportion of 0.1 - 2 wt.%,
- yttrium (Y) in a proportion of 0.1 - 1 wt.%,
- hafnium (Hf) in a proportion of 1 - 5 wt.%,
- palladium (Pd) in a proportion of 0.5 - 5 wt.%,
- boron (B) in a proportion of 0.5 - 2.5 wt.%, and
- nickel (Ni) in a residual proportion such that the sum of all portions yields 100 wt.%.

By alloying silicon (Si) in a proportion of 0.1 to 1 wt.%, the melting point of the solder alloy may be lowered further in combination with the palladium, boron and yttrium.

Example embodiments of the present invention are are described in more detail below in the following description.

DETAILED DESCRIPTION

Example embodiments of the present invention relate to the use of a soldering method for repairing thermodynamically stressed components of a gas turbine, for example of guide blades of an aircraft engine or also of a stationary gas turbine. Example embodiments of the present invention relate not only to the soldering method itself, but rather also to the provision of a solder alloy or a multi-component soldering system as well as to a use of the solder alloy and the multi-component soldering system. The solder alloy and the multi-component soldering system are suitable both for repairing turbine components, which are manufactured from a polycrystalline alloy, as well as for turbine components that are manufactured from a directedly solidified or monocrystalline alloy. Using the soldering method or solder alloy or multi-component soldering system makes it possible to achieve sufficiently high mechanical properties in the soldered regions of the gas turbine components such as, e.g., the fatigue-resistances such that the structural integrity of the relevant component of a gas turbine is maintained. Furthermore, improved oxidation and corrosion properties may be achieved in the soldered regions as compared to those regions that are repaired using conventional soldering methods.

The solder alloy is a nickel-based alloy and in addition to nickel (Ni) includes at least also chromium (Cr), cobalt (Co) and molybdenum (Mo). The tungsten (W) used in conventional solder alloys is largely replaced by molybdenum (Mo). This may increase the strength of the repaired region by mixed crystal hardening of the γ-nickel matrix without raising the melting point of the solder alloy.

In addition to nickel (Ni), chromium (Cr), cobalt (Co) and molybdenum (Mo), the solder alloy includes palladium (Pd) as well as yttrium (Y). Both palladium (Pd) as well as yttrium

(Y) may lower the melting range of the solder alloy into a range of 1050°C to 1200°C and simultaneously may improve the oxidation properties of the solder alloy or of the soldered region. Palladium (Pd) may be limited to a maximum portion of 5 wt.% since it may make the solder material much more expensive if it is alloyed in excessively high concentrations.

Another element that may be included in the solder alloy is boron (B). Like palladium (Pd) and yttrium (Y), boron (B) may lower the melting range of the solder alloy into a range of 1050°C to 1200°C and may be limited to a maximum portion of 2.5 wt.%. By limiting boron (B) to a maximum of 2.5 wt.%, it is possible effectively to limit the boride phase portion in the soldered regions, which has an embrittling effect.

Furthermore, the solder alloy may include a suitable proportion of aluminum (Al), tantalum (Ta) and niobium (Nb) in addition to the above-mentioned elements. The portion of aluminum (Al) may be between 2 and 8 wt.%. In the solder alloy, tantalum (Ta) is included in a proportion of 1 to 8 wt.% and niobium (Nb) is included in a proportion of 0.1 to 2 wt.%. By alloying γ'-phase-forming elements such as tantalum (Ta), niobium (Nb) and aluminum (Al), additional mechanical strength by particle hardening may be achieved in the soldered regions in addition to the already described mixed crystal hardening.

In addition, the solder alloy may include hafnium (Hf) in a proportion of 1 to 5 wt.%. The use of hafnium may have a positive effect on the wetting and flow properties of the molten solder alloy and the oxidation-resistance of the repaired regions of the respective component. The portion of hafnium (Hf) is limited to the specified maximum value of 5 wt.% in order to limit the portion of the hafnium-containing

hard phases in the soldered regions, which have an embrittling effect.

In addition, the solder alloy may include silicon (Si) in a proportion of 0.1 to 1 wt.%. The addition of silicon (Si) is able to support and strengthen the melting point-reducing effect of the palladium (Pd), yttrium (Y) and boron (B), without increasing the boride phase portion in the repaired regions of the component.

The solder may have the following composition:

chromium (Cr) in a proportion of 5 - 17 wt.%,
cobalt (Co) in a proportion of 8 - 15 wt.%,
molybdenum (Mo) in a proportion of 1 - 5 wt.%,
aluminum (Al) in a proportion of 2 - 8 wt.%,
tantalum (Ta) in a proportion of 1 - 8 wt.%,
niobium (Nb) in a proportion of 0.1 - 2 wt.%,
yttrium (Y) in a proportion of 0.1 - 1 wt.%,
hafnium (Hf) in a proportion of 1 - 5 wt.%,
palladium (Pd) in a proportion of 0.5 - 5 wt.%,
boron (B) in a proportion of 0.5 - 2.5 wt.%,
silicon (Si) in a proportion of 0.1 - 1 wt.%,
nickel (Ni) in a residual proportion such that the sum of the portions yields 100 wt.%.

The solder alloy may have the following composition:

chromium (Cr) in a proportion of 9 - 11 wt.%,
cobalt (Co) in a proportion of 9 - 11 wt.%,
molybdenum (Mo) in a proportion of 3.5 - 4.5 wt.%,
aluminum (Al) in a proportion of 3.5 - 4.5 wt.%,
tantalum (Ta) in a proportion of 1.5 - 2.5 wt.%,
niobium (Nb) in a proportion of 0.5 - 1.5 wt.%,
yttrium (Y) in a proportion of 0.1 - 0.5 wt.%,
hafnium (Hf) in a proportion of 3.5 - 4.5 wt.%,
palladium (Pd) in a proportion of 3.5 - 4.5 wt.%,

boron (B) in a proportion of 1.5 - 2.0 wt.%,

nickel (Ni) in a residual proportion such that the sum of the portions yields 100 wt.%.

The solder alloy may be particularly suitable for use in repairing guide blades of an aircraft engine, the guide blades being made either from a polycrystalline or a directedly solidified or monocrystalline alloy. Following the repair of the relevant regions of the gas turbine using the solder alloy, the soldered regions may have mechanical properties that correspond as much as possible to the material of the undamaged guide blade. The solder alloy is adapted specifically for the purpose of repairing engine components.

The solder alloy may have optimized melting properties, flow properties and wetting properties as well an optimized ability to fill cracks.

The effect of the melting point-lowering elements yttrium (Y) and palladium (Pd) on the melting range of the solder alloy is made clear by the following calorimetric measurements.

In the following, four solder alloys A2, A3, A5 and A10 are compared. (For composition see Table 1).

Table 1: Compositions of the solder alloys, concentrations in percentages by weight.

Solder alloy	Ni	Cr	Co	Mo	Al	Ta	Nb	Y	Hf	Pd	B
A2	Bal.	10	10	4	4	2	1	0.5	4	4	1.8
A3	Bal.	10	10	4	4	2	1	0	0	4	1.8
A5	Bal.	10	10	4	4	2	1	0.5	0	0	1.8
A10	Bal.	10	10	4	4	2	1	0	4	0	1.8

Following the melting of the solder alloys in an arc furnace into blocks weighing approximately 10g, specimens of a mass of 50-70 mg are taken from these blocks for the calorimetric

measurements. Using DSC (differential scanning calorimetry), the melting behavior of the individual solder alloys is investigated in these specimens. A Netsch DSC 404 unit is used as a calorimeter.

Table 2 shows the solidus and liquidus points of the examined solder alloys A2, A3, A5 and A10 determined by the DSC analysis.

Table 2: Melting Ranges of the Solder Alloys

Solder alloy	T solidus/°C	T liquidus /°C
A2	1059	1196
A3	1010	1254
A5	1039	1249
A10	1068	1244

The solidus and liquidus point listed in Table 2 illustrate the effect of the melting point-lowering elements Y and Pd used in addition to the element boron.

Solder alloy A10 has neither Y nor Pd in addition to boron, and accordingly has the highest solidus temperature 1068°C and a liquidus temperature of 1244°C.

Solder alloy A5 includes 0.5 wt.% of Y, but no Pd. Compared to A10, A5 has a reduced solidus temperature of 1039°C, although at 1249°C its liquidus temperature is even somewhat higher than A10.

A similar effect occurs in A3, which includes Pd at 4 wt.%, but no Y.

If Y and Pd are specifically combined as in solder alloy A2, then both the solidus temperature (1059 °C) as well as the liquidus temperature (1196 °C) are reduced as compared to A10. This has the consequence that in the case of A2, at 137°C, the

melting range as the difference between the liquidus point and the solidus point is lowest in comparison to the other solder alloys. This may be advantageous to the extent that a low melting range allows for a quick and complete melting of the solder alloy when heated. This may prevent a segregation of the melting solder alloy and at the same time may ensure an optimum wetting and crack-filling performance.

For this reason, the combination of the two alloy elements yttrium and palladium and their use, in addition to boron, as melting point-reducers in the solder alloy may be particularly advantageous.

Up to this point in time, no solder alloy optimized in its composition in this manner is believed to be conventional.

The soldering temperature of the solder alloy described here is adjusted to the different solution annealing temperatures of the polycrystalline or directedly solidified or monocrystalline alloys.

The multi-component soldering system includes the solder alloy, as already described above, and additionally of at least one additive material. The multi-component soldering system is obtained by mixing the solder alloy and the additive material, the mixing not having to be limited to the powdery components.

In order to be able to apply the powdery components of the multi-component soldering system onto the regions to be repaired, these components are mixed with a binder. The resulting paste is applied with the aid of a sprayer or with the aid of a spatula onto the regions to be repaired. The proportion of the binder in the multi-component soldering system amounts to 1-15 wt% of the powdery components.

The additive materials are metal powders of an alloy, the melting range of which is above the melting range of the solder alloy. The additive materials may be nickel-based or cobalt-based alloys. A specific mixing of the solder alloy with the additive materials, a multi-component soldering system is provided, which may be especially adapted to a material of a component to be repaired, e.g., of a guide blade of a turbine. Accordingly, the multi-component soldering system is made up of a variable powder quantity of the solder alloy having at least one additive material, the mixture ratio of the solder alloy and the additive material being freely selectable.

May be provided are additive materials, namely, a metal powder, which in addition to nickel (Ni) also include one or more of the following elements:

chromium (Cr) in a proportion of up to 30 wt.%,
cobalt (Co) in a proportion of up to 20 wt.%,
tungsten (W) in a proportion of up to 15 wt.%,
molybdenum (Mo) in a proportion of up to 10 wt.%,
aluminum (Al) in a proportion of up to 10 wt.%,
tantalum (Ta) in a proportion of up to 10 wt.%,
titanium (Ti) in a proportion of up to 10 wt.%,
rhenium (Re) in a proportion of up to 10 wt.%,
iron (Fe) in a proportion of up to 5 wt.%,
niobium (Nb) in a proportion of up to 5 wt.%,
yttrium (Y) in a proportion of up to 5 wt.%,
hafnium (Hf) in a proportion of up to 5 wt.%,
palladium (Pd) in a proportion of up to 5 wt.%,
carbon (C) in a proportion of up to 1 wt.%,
zirconium (Zr) in a proportion of up to 1 wt.%,
boron (B) in a proportion of up to 1 wt.%,
silicon (Si) in a proportion of up to 1 wt.%.

The additive material may have the following composition:

chromium (Cr) in a proportion of 13.7 - 14.3 wt.%,
cobalt (Co) in a proportion of 9 - 10 wt.%,
tungsten (W) in a proportion of 3.7 - 4.3 wt.%,
molybdenum (Mo) in a proportion of 3.7 - 4.3 wt.%,
aluminum (Al) in a proportion of 2.8 - 3.2 wt.%,
titanium (Ti) in a proportion of 4.8 - 5.2 wt.%,
carbon (C) in a proportion of 0.15 - 0.19 wt.%,
zirconium (Zr) in a proportion of 0.03 - 0.1 wt.%,
boron (B) in a proportion of 0.01 - 0.02 wt.%,
nickel (Ni) in a residual proportion such that the sum of the portions yields 100 wt.%.

The mechanical properties of the multi-component soldering systems made up of the solder alloy and the additive material may ensure that the solder structures in the repaired regions have, on the basis of their static and cyclical strength, a sufficiently high resistance with respect to the thermal and mechanical stresses in the gas turbines.

For this purpose, the following hot tensile tests and fatigue tests (LCF) are conducted.

The tests described are performed on a select multi-component soldering system, which is characterized by a good melting behavior and a good ability to fill cracks. For this purpose, solder alloy A2 is mixed with an additive material M1 at a mixture ratio of 1:1 (percentage by weight), M1 having the following composition:

chromium (Cr) in a proportion of 13.7 - 14.3 wt.%,
cobalt (Co) in a proportion of 9 - 10 wt.%,
tungsten (W) in a proportion of 3.7 - 4.3 wt.%,
molybdenum (Mo) in a proportion of 3.7 - 4.3 wt.%,
aluminum (Al) in a proportion of 2.8 - 3.2 wt.%,
titanium (Ti) in a proportion of 4.8 - 5.2 wt.%,

carbon (C) in a proportion of 0.15 - 0.19 wt.%,
zirconium (Zr) in a proportion of 0.03 - 0.1 wt.%,
boron (B) in a proportion of 0.01 - 0.02 wt.%,
nickel (Ni) in a residual proportion such that the sum of the portions yields 100 wt.%.

The hot tensile tests are conducted at a temperature of 871°C ±3°C. Using a radiation furnace, the specimens are heated such that a homogeneous temperature distribution may be ensured across the entire sample. The tests are conducted in a servohydraulic machine. The extension rate may be 0.93 mm/min such that the tests must be classified as displacement-controlled.

Flat tensile specimens from the DS alloy René-142 having a cross section of 6.35 x 1.5 mm and a measurement path of 25.4 mm are used as specimens. The flat specimens may be preferred to the round specimens used otherwise since in terms of their dimensions they more closely approximate the case of application, emulating the thin-walled blade of a turbine guide blade having a wall-thickness of 1.5 mm.

In each case, three specimens are tested having traversing soldering gaps of a width of 0.25 mm, 0.5 mm and 1.0 mm, which are soldered or filled up using the described multi-component soldering system A2/M1.

Table 3 shows the averages of hot tensile strengths (UTS) as well as the UTS values of the nickel-based alloys René-80 (polycrystalline) and DS René-142 (directedly solidified) as basic material data.

Table 3: Hot tensile strengths (UTS) of the multi-component soldering system A2/M1 for different gap widths

Soldering system	Gap / mm	UTS / MPa
A2/M1	0.25	643
	0.50	519
	1.00	547
	René - 80	648
	René - 142 DS	858

Table 3 shows that multi-component soldering system A2/M1 has remarkably good hot tensile properties.

For a gap width of 0.25 mm, the hot tensile strength (UTS) of A2/M1 corresponds to the value of the base material René-80, which corresponds to a UTS value of 75% of DSR142. Even at a gap width of 0.5 mm and 1.0 mm, 80% (with respect to René-80) or 60% (with respect to René-142) of the hot tensile strength (UTS) are still achieved.

The hot tensile tests provide guide values for the strength properties of the solder structures. The results of the LCF tests are more meaningful since they more closely reflect the actual thermomechanical alternating stress of the gas turbine components.

The test temperature of the LCF tests is 982°C +/-10°C, the flat specimens made of the DS alloy René-142 heated inductively. The flat tensile specimens have a cross section of 9.53 x 1.55 mm and a measuring path of 12.7 mm. The test is conducted as an axial, force-controlled tensile threshold test having a sinusoidal stress characteristic. For this purpose, 20 cycles/min at a ratio of stress amplitude/average stress of 0.95 are applied to the specimen.

As in the hot tensile tests, at different maximum stresses, flat specimens are used multi-component soldering system A2/M1 having three traversing soldering gaps of 0.25 mm, 0.5 mm and 1.0 mm.

Average values are in Table 4.

Table 4: LCF data (average values) of the multi-component soldering system A2/M1 for different gap widths and maximum voltages.

Soldering system	Gap width/mm	Max. voltage/MPa	Load changes
A2/M1	0.25	152	50244
		173	6729
		207	4626
		241	702
A2/M1	0.5	152	9146
		173	11785
		241	949
A2/M1	1,0	152	9679
		173	4406
		207	842
		241	454
René - 142 DS		311	13243
		345	7369
		380	2793
		414	1283
René - 80		283	5000
		276	7000
		262	10000
		255	30000

Table 4 shows that multi-component soldering system A2/M1 has remarkably good fatigue properties.

Like the hot tensile tests, the LCF tests show a dependency of the fatigue or tensile threshold strength on the gap width of the solder structures. For a load change number of 5000 cycles as a typical value for LCF tests, the fatigue strength of the A2/M1 solder structures for gap widths of 0.26 mm and 0.5 mm amounts to 65-70% of the value of the René-80 base material or 50-55% of the value of the René-142 base material. For a gap width of 1.0 mm, only a low decline to 60% (with respect to René-80) or 48% of the fatigue strength of the base material (with respect to René-142) is ascertained.

The fatigue strengths or tensile threshold strengths of multi-components soldering system A2/M1 are higher than conventional multi-component soldering systems.

Using the solder alloy hereof or the multi-component soldering system hereof, a method may be provided for processing, e.g., repairing, workpieces, that is, for processing guide blades of an aircraft engine. The workpieces may be manufactured from a polycrystalline or directedly solidified or monocrystalline alloy.

The method is based on high-temperature diffusion soldering using the solder alloy hereof or using the multi-component soldering system hereof. This is a repair method. The high-temperature diffusion soldering occurs under the following conditions:

- heating under vacuum or protective gas to a temperature of 1200 - 1260°C with a subsequent holding time of 15 - 60 min,
- cooling under vacuum or protective gas to a temperature of 1100 - 1140°C with a subsequent holding time of approximately 240 min,
- cooling under vacuum or protective gas to a temperature of 1080 - 1120°C with a subsequent holding time of approximately 60 min.

The high-temperature diffusion soldering may be followed by the following heat treatment: Heating under vacuum or protective gas to a temperature of 1065-1093°C with a subsequent holding time of approximately 240 min, this, e.g., occurring in the context of a coating process.

Furthermore, the high-temperature diffusion soldering may be followed by the following heat treatment: heating under vacuum or protective gas or ambient atmosphere to a temperature of

871-927°C with a subsequent holding time of 60 - 960 min, this, e.g., occurring in the context of an aging process.

The use of the solder alloy and of the multi-component soldering system is not limited to pure repair methods. Rather, the solder alloy and the multi-component soldering system are generally also applicable for joining processes. Due to the mixing ratio of the solder alloy and possibly additive materials optimized for repair purposes, however, the use in the repair of guide blades of an aircraft engine may be particularly advantageous.